

PCT/EP00/07174
21 JAN 2002BREAKING OF OIL/WATER EMULSION

The invention is related to a process for breaking an emulsion of bituminous oil and water into the respective bituminous oil and water phases.

5 In the Orinoco Basin, in Trinidad, in North America, and in other areas, deposits of heavy oil and asphalt occur which are noted for their high bitumen content. These natural substances -which resemble oil and are commonly known as bituminous oil- can only be extracted by processes reducing viscosity and not by standard refinery methods. The extraction method currently used in the Orinoco Basin comprises emulsification of the bituminous oil at bed level, extraction of the emulsion, upgrading and transport.

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20 Emulsifying the bituminous oils with water brings about a considerable reduction in the viscosity of these oils. The original viscosity in excess of 300 Pa.s at 20 °C is reduced to the range of 12 to 35 Pa.s as a consequence of emulsification. It is only this viscosity-reducing process that permits the extraction, transport and further processing of bituminous oil. Owing to the relatively high bitumen content, the bituminous oil cannot be easily processed by traditional refinery methods.

25 At present, the bituminous oil emulsion is used to fire power stations. The high sulphur content in bituminous oils (from 3 to 4%) causes a correspondingly high level of environmental pollution, a level which is becoming more and more unacceptable in the industrialised countries. The alternative is to produce desulphurized fuel gas by partial oxidation, also referred to as gasification, of the bituminous oil, thus obtaining raw

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gas mainly consisting of CO and H₂. The raw gas is subsequently treated to obtain desulphurized fuel gas suitable for firing combined cycle power plants. The partial oxidation of bituminous oil is also suitable for the generation of synthesis gas or hydrogen, which can be used in a Fischer-Tropsch process or in processes for preparing a wide range of chemicals such as methanol, ammonia, oxy-products, formic acid and acetic acid.

EP-A-790292 describes a process in which an emulsion of Olinoco tar and water, also containing small amounts of sulfonic acid type surface active agent, having a starting temperature of 20 to 30 °C is broken by raising the temperature of the emulsion to 150 °C in two stages by means of an indirect heat exchange.

US-A-5441548 also describes a process in which a bituminous oil/water emulsion is broken by raising the temperature of the emulsion to a temperature of between 130 and 170 °C by means of two heat exchangers in series. The water and bituminous oil phase are subsequently separated by means of phase separation in a gravity type emulsion separator. According to the specification no additional chemicals such as for example demulsifiers are added to improve the separation of the bituminous oil phase and the water phase.

A disadvantage of the above processes is that the starting emulsion still has a relatively high viscosity at a temperature of below 100 °C when entering the first heat exchanger. Because of this high viscosity the heat exchanger must be equipped with large diameter tubes through which the emulsion flows and/or a high pressure must be applied to overcome the pressure drop in the first part of the heat exchanger where the viscosity is still high. Large diameter tubes are less effective resulting in that the heat exchanger will become large in

order to perform the desired raise in temperature or, as is the case in US-A-5441548, more than one heat exchanger will have to be used in series. The high pressure needed is disadvantageous because special pumps must be used.

5 Furthermore the heat exchanger and the process equipment downstream of the heat exchanger, like for example the gravity-type emulsion separator, must be designed for this higher pressure level for obvious safety reasons. The present invention provides a process, which can be
10 operated at a lower pressure having all the obvious advantages in view of the above.

The following process achieves this object. Process for separating an emulsion of a bituminous oil and water into a liquid water phase and a liquid bituminous oil
15 phase, wherein the following steps are performed:

(a) raising the temperature of the bituminous oil/water emulsion having a temperature of below 100 °C to a temperature of above 140 °C, and

(b) performing a phase separation wherein a liquid
20 water phase and a liquid bituminous oil phase are obtained,

wherein the heating of the emulsion in step (a) is effected by first mixing part of liquid bituminous oil phase obtained in step (b) having a temperature of above
25 140 °C with the bituminous oil/water emulsion and subsequently raising the temperature of the resulting mixture to a temperature of above 140 °C by making use of indirect heat exchange means.

It has been found that by mixing the emulsion feed
30 with part of the bituminous oil phase obtained in the phase separation of the emulsion the temperature can be sufficiently raised in order to lower the viscosity of

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the mixture entering the heat exchanger means. This results in that a lower pressure drop in the heat exchanger has to be overcome enabling a lower inlet

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pressure. Accordingly smaller and more simple pumps, smaller heat exchanger means and process equipment designed for lower pressure levels can be used with the process according the invention.

5 Applicants have also found that the temperature at which step (b) is performed is important for an efficient process. Applicants found that for this oil-water system the water phase has a higher density than the oil phase at temperatures of below about 130 °C. Above about 130 °C
10 the oil phase has a higher density than the water phase. By increasing the temperature starting from about 130 °C the difference in density increases and thus the ease at which the phases separate in a heavy oil phase and a lighter water phase increases. At 140 °C a sufficient
15 difference is achieved to perform a phase separation. Preferably the temperature is not higher than 200 °C because at higher temperatures the solvability of the oil in water and water in oil becomes undesirably high. A more preferred range is between 160-200 °C in which the
20 difference in density is sufficiently high to achieve a efficient phase separation and the solvability is of water in oil and oil in water is within an acceptable range. Most preferably the temperature is between 160-180 °C. The weight ratio of oil phase and emulsion
25 which are mixed to achieve the first raise in temperature is preferably between 1 to 2 and 1 to 5...

Suitable indirect heat exchanger means to be used in the process according to the invention can be for example those means disclosed in US-A-5441548. An example of a
30 preferred heat exchanger means is a shell-tube heat exchanger, wherein a hot medium, like for example steam or hot oil, at the shell side exchanges its heat with the mixture comprising the emulsion present at the tube side. The temperature rise in the heat exchanger means is

preferably from between 120-150 °C to a value between 160-180 °C.

For some applications of the bituminous oil obtained by the process according to the invention it is
5 advantageous to lower the level of water soluble salts in said oil. Examples of such salts are magnesium, calcium, sodium, potassium, containing salts. Such salts may cause severe fouling in for example the process equipment of a partial oxidation process. In for example the process
10 disclosed in US-A-5441548 the content of such water soluble salts in the bituminous oil phase will be too high for these applications. Applicants have now found that by lowering the pH of the water phase obtained in step (b) to a level of below 7 a lower content of these
15 salts remain in the oil phase. The pH is preferably between 4 and 6. Preferably the pressure during phase separation is sufficiently high to ensure that the water phase is obtained as a liquid in step (b). Suitable pressures are between 5 and 20 bars. Obtaining the water
20 phase as a liquid further ensures that most salts will be removed with the water phase. The improved removal of these water soluble salts by lowering the pH of the water phase is preferably used in combination with the process according to the invention. It must be appreciated that
25 this technical measure can also be used in a more general manner and not only limited as an embodiment of the present invention in which the recycling of part of the oil is an essential feature. Typical emulsions which can be treated by the above preferred embodiment may have a
30 calcium content of above 20 ppmw and/or a magnesium content of above 20 ppmw.

Typically the bituminous oil/water emulsion has a water phase with a pH of above 7 caused by the natural and/or the added surfactants present in the emulsion. In
35 order to achieve the lower pH suitably an acid is added

prior to phase separation. Examples of suitable acids which may be used are those acids which do not cause significant problems in the water treatment facilities in which the water phase is suitably further treated before being returned to surface water, like rivers, sea or lakes. Examples of such acids are sulphuric acid, phosphoric acid and acetic acid of which sulphuric acid is preferred because of its availability and ability to simply be removed from the water phase, for example as gypsum. The amount of acid added can be easily determined by measuring the pH of the water phase obtained in the process.

Phase separation can be performed in any conventional phase separation device known to one skilled in the art. These devices can be a gravity-type separator or a combination of a gravity separator and a down stream emulsion separator in the electrostatic field.

The bituminous oil can be the natural occurring crude petroleum sources found in the Orinoco Basin, in Trinidad, in North America, and in other areas, which are noted for their high bitumen content. The bituminous oil may also be the vacuum residue fraction obtained when refining a typical petroleum crude. Due to for example local environmental reasons it may happen that these fractions cannot be further processed to fuels. It may be desirable to transport these fractions to locations where they may be used as gasification feedstock. Due to their viscous properties these fractions will be suitably transported as a water/oil emulsion.

The bituminous oil/water emulsion may also comprise surfactants. Examples of possible surfactants are ethoxylated alkyl phenols, for example nonyl phenol ethoxylate compounds, ethoxylated alcohols, water soluble amine compounds, alkali compounds and combinations thereof. Examples of water soluble amines are ethylamine,

diethylamine, triethylamine, n-butylamine, tri-
isobutylamine, dimethylamine, methylamine, propylamine,
dipropylamine, sec-propylamine, butylamine, sec-
butylamine, ethanolamine and mixtures thereof. The
5 ethoxylated alcohols may contains between 12-18 carbon
atoms, for example polyethoxylated tridecanol. Examples
of alkali compounds are sodium chloride, potassium
chloride, sodium nitrate, potassium nitrate, calcium
nitrate, magnesium nitrate and mixtures thereof. The
10 emulsion typically comprises between 60-85% by weight of
the bituminous oil, between 0.01 to 5% by weight of
surfactant and between 10 to 40% by weight of water.
Examples of bituminous oil water emulsions optionally
comprising the exemplified surfactants, which can be used
15 in the process according to the present invention are for
example described in US-A-5419852, US-A-5437693,
US-A-5480583, US-A-5503772, US-A-5556574, US-A-5603864
and US-A-5622920. Preferred emulsion are ORIMULSION and
OLIMULSION as for example described in US-A-4795478 or
20 EP-A-790292 respectively (ORIMULSION is a trademark of
Intevep S.A. Venezuela) (OLIMULSION is a trademark of
Bitumes Olinoco S.A. Venezuela).

The bituminous oil obtained in the above process can
be advantageously be used as feedstock for a gasification
25 process. The gasification process can be any process
known in the art which is suitable for processing heavy
feedstocks like the above described bituminous oil.
Examples of such processes are the SHELL Gasification
Process as for example described by Heurich et al. in
30 "Partial Oxidation in the Refinery Hydrogen Management
Scheme", AIChE 1993 Spring Meeting, Houston,
30 March 1993 and the TEXACO process as described in
Petroleum Review June 1990, page 311-314. Typically the
bituminous oil and oxygen or air is fed to a gasification
35 burner. Optionally a moderator gas, for example steam or

carbon dioxide, may be supplied to the burner as well. At the burner outlet the reactants are atomised and mixed and an exothermic partial oxidation takes place at a temperature of between 1300 and 1500 °C. The pressure is typically between 10 and 90 bar. The resulting fuel or synthesis gases will mainly consist of CO and H₂. Other components will be CO₂, CH₄, H₂O, H₂S, COS, N₂ and Ar. The hot fuel gases are subsequently lowered in temperature for example by means of a water quench or by means of indirect heat exchange. An example of such an indirect heat exchange method is described in EP-A-774103 and which describes a vertical oriented shell-tube heat exchanger in which the temperature is typically lowered from 1300-1500 °C to a temperature typically between 300 and 350 °C. In such a device high pressure steam is generated at the shell side of the unit while the synthesis gases are lowered in temperature at the tube side of the heat exchanger. The advantages of the invention are even more achieved when the bituminous oil obtained by the present invention is used in a gasification process which applies such an indirect heat exchanger. This is because the water soluble salt in the feedstock, which salts are effectively removed by one preferred embodiment of the present invention, can cause severe plugging of the heat exchanger (tubes).

The invention will be illustrated by making use of Figure 1. Figure 1 describes a process for separating a bituminous oil/water emulsion and the gasification of the bituminous oil thus obtained. A bituminous oil/water emulsion (1) is mixed with a recycle stream of bituminous oil (8) resulting in stream (2). This mixture (2) is heated to the desired temperature in heat exchanger (3) resulting in heated stream (4) which is fed to the gravity phase separator (5). In gravity-type

separator (5) a water phase (6) as the top phase and a heavier bituminous oil phase (7) as the bottom phase is obtained. Part of the bituminous phase (7) is recycled via pump (9) to heat exchanger (3) as stream (8) to which recycle stream some acid is supplied via stream (10) in order to lower the pH to the desired level. The remaining part (11) of the bituminous oil phase (7) is fed to gasification unit (14). To this reactor unit comprising burners (not shown) also air or oxygen is fed via (12) and optionally a moderator gas is fed via (13). The fuel gas mixture obtained via (15) is lowered in temperature in a shell-tube heat exchanger (16) to which boiler feed water is supplied to via (17) and high pressure steam (18) is generated. Fuel gas mixture (19) obtained in heat exchanger (16) is further processed in downstream unit operations (not shown) in which for example ash and soot and sulphur containing compounds are removed.

The invention will be illustrated by the following non-limiting example.

Example 1

785 ton/day of ORIMULSION having a temperature of 40 °C was contacted with 3140 ton/day of recirculating oil phase having a temperature of 170 °C at 15 bar resulting in a mixture having a temperature of 149.5 °C. This mixture was further heated in a heat exchanger to a temperature of 170 °C having a viscosity of 179 cSt. Phase separation was performed resulting in 236 ton/day water and 3690 ton/day oil phase at 10 bar of which oil phase 3140 ton/day is used to heat the Orimulsion feed and 550 ton/day is obtained as oil product having a temperature of 170 °C and a viscosity of 102 cSt. The pressure of the circulating oil phase is raised from 10 bar to 15 bar by means of a pump. To this circulating mixture 63 kg/day of sulphuric acid is added.

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Example 2

To one weight part of a typical ORIMULSION (ORIMULSION is a trade name of Intevep S.A. describing an emulsion of a bituminous oil and water and their preparation is described in US-A-4795478) an amount of sulphuric acid was added in order that the pH of the resulting water phase had a pH of 5 (80 mg sulphuric acid per kg of emulsion). The water content of the emulsion was 30% by weight. Phase separation was performed at a temperature of 180 °C and at a pressure of 10 bar. The phases remained in the liquid phase during phase separation. A water phase was obtained as the top phase. In Table 1 some more information of the ORIMULSION used and the resulting phase separation is presented.

Example 3

Example 2 was repeated except that no acid was added. The pH of the resulting water phase was 7.9. See also Table 1.

Table 1

	Orimulsion	Example 2 Bituminous oil phase	Example 3 Bituminous oil phase
Calcium (ppmw)	34	12	52
Magnesium (ppmw)	46	5	46
oil in water phase after phase separation (wt%)	-	0.1	0.3

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